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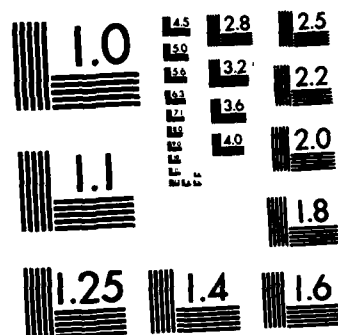|					
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ELECTRICAL RELAXATION IN PURE AND ALKALI METAL-

THIOCYANATE COMPLEXED POLY(ETHYLENE OXIDE)

by

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ELECTRICAL RELAXATION IN PURE AND ALKALI METAL-

THIOCYANATE COMPLEXED POLY(ETHYLENE OXIDE)

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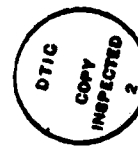
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ABSTRACT

Audio frequency complex admittance and DSC studies have been performed on pure poly(ethylene oxide)(PEO) and PEO complexed with alkali metal thiocyanates over the temperature range 5.5-380K. The dielectric constant of the complexed materials is found to be greater than for pure PEO. A discontinuity in the conductivity is found which increases in temperature as the size of the cation increases. In every case, the discontinuity is associated with a feature in the DSC results. Next, some evidence is given that water may enhance the formation of amorphous complexed PEO. In pure PEO, α_a and γ relaxations are observed in good agreement with previous work. A thermal anomaly is found corresponding to α_a. In addition, α_c is identified in pure PEO. Very little difference is found for the γ relaxation between pure PEO and PEO-NaSCN. For PEO-KSCN, three distinct peaks are found in the γ relaxation region. These results are consistent with a $tg^{\pm}t \rightleftharpoons tg^{-}t$ transition interpretation for γ where the cations reside within the helical channels at low temperatures.

GAMMA

ALPHA SUB A

ALPHA SUB C

2

1. INTRODUCTION

Ion conducting poly(ethylene oxide) (PEO) has been attracting a great deal of attention because of possible applications as a solid state electrolyte (1-18). As electrical relaxation has proved a useful technique in the study of polymers, such studies of PEO complexed with various thiocyanates were undertaken and the results are presented in the present work.

2. EXPERIMENT

Audio frequency measurements of the capacitance, C, and the conductance, G, divided by the frequency, were performed using a fully automated, microprocessor controlled bridge constructed by one of the authors (C.G.A.). The bridge balances the sample against a known capacitance and resistance in parallel. It operates at the five frequencies given by $\log(f)=$ 2, 2.5, 3, 3.5 and 4 with f in Hz. The bridge is at least as sensitive and accurate as the best commercially available manual bridge.

The measurements were performed in a Cryogenics Associates temperature controlled dewar with an eight sample holder. The eight sample holder allows essentially simultaneous measurement of eight different specimens, thus allowing a useful comparison of materials. The data were taken with the temperature held constant with approximately one hour allowed for equilibration at high temperatures decreasing to about 20 minutes at the lowest temperatures. Above 45K the temperature is measured using a Rosemount Eng. Co. platinum resistance thermometer and below 45K it is measured using a CryoCal Inc. germanium resistance thermometer. The temperature is controlled using a 27 Hz feedback temperature controller and in general was controlled to within 0.001K. The absolute temperature is probably accurate only to about 0.1K. Other results obtained using this system are given elsewhere (19-24).

Films of PEO (Polysciences, MW $5x10^6$) complexed with various salts were obtained by preparing solutions of the materials and casting the liquid on a teflon plate. The films were degassed and air dried. All operations were performed at room temperature though the dissolution of the salts was usually performed

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at about 70C. The proportion of polymer repeat
unit to salt was 4.5 to 1 for NaSCN and KSCN and
5 to 1 for LiSCN. The films were finally vacuum
dried at 60C for about 24 hours. In addition,
the samples are actually dried a second time
under vacuum in situ since all measurements are
performed under vacuum and initially the
temperature is increased to about 100C. This
procedure takes place over about 10 hours. In
some cases acetonitrile was used as the solvent,
but in general, methanol proved to be more
effective.

The samples were disks ranging from 0.25 to
1 mm thick and about 1.5 cm in diameter.
Aluminum electrodes were evaporated onto the
surfaces. While one electrode covered one full
surface, the other electrode was only about 0.9
cm in diameter for convenience of loading into
the sample holder, which was originally designed
for other purposes.

This procedure limits the accuracy of the
complex dielectric constant, $\varepsilon^* = \varepsilon' - j\varepsilon''$, or the
conductivity, σ, since the usual equations:

$$C = \frac{\varepsilon_0 \varepsilon' A}{d} \qquad (1)$$

or

$$G = \frac{\sigma A}{d} \qquad (2)$$

are not strictly applicable because of the
geometry. ε_0 is the permittivity of free space
and A and d would be the area and thickness of a
perfect parallel plate specimen. However, since
absolute conductivities are not the primary
subject of the present paper, eqs. (1) and (2)
were applied anyway using the average area of
the two faces for A. Further, no thermal
expansion correction factor was included because
of an apparent lack of literature values for PEO.
The geometrical factor, A/d, was only measured
at room temperature and ε' at 300K and 1000 Hz
calculated from eq. (1). The values of ε' at all
other frequencies and temperatures were
calculated assuming that ε' varies as the
capacitance. The values of ε'' were then
calculated from:

$$\varepsilon'' = \frac{\varepsilon' G}{\omega C} \qquad (3)$$

and the conductivity was obtained from:

$$\sigma = \varepsilon_0 \varepsilon'' \omega. \qquad (4)$$

These procedures place the absolute accuracy at
about 10%. However, the relative uncertainty in
ε' or σ is far better since both G/ω and C are
measured to about 1 aF for values up to 10 pF
and to five significant figures above that.

Differential scanning calorimeter (DSC) measurements were carried out using a Perkin Elmer DSC-1B instrument. The measurements were performed over the temperature range 190-450K at a rate of 10C per minute. The instrument has a 15C maximum temperature error over the range studied.

3. RESULTS AND DISCUSSION

The results for ε' and ε'' or σ at three frequencies are shown in figs. (1)-(4) along with the significant portions of the DSC traces for the pure and complexed materials. For clarity, the electrical data are shown for decreasing temperatures only and the lines connect the datum points. To show a typical distribution of datum points, one complete set of 1000 Hz results are plotted in fig. (5).

In general, the low temperature values of ε' for the complexed materials are found to be higher than for pure PEO. The difference is attributed primarily to the polarization of the "ionic sublattice" at low temperatures.

The results for the high temperature conductivity plotted in figs. (2d), (3d), and (4d) show varying amounts of dispersion. The apparent lower conductivity for lower frequencies and high temperatures is attributed to blocking electrode effects. However, in all cases, there is very little difference (usually less than 1%) between values of σ at $10^{3.5}$ and 10^4 Hz and thus the values at 10^4 Hz well represent the conductivity of the samples. Further evidence for this assertion is given in figs. (3d) and (4d) where the results of Wright (2) are plotted in addition to the results of the present work. The agreement is quite good considering the uncertainty in the data and other possible variations such as sample preparation technique or water content.

3.1. Pure PEO

The results for a methanol based pure PEO sample are shown in fig. (1). The results for acetonitrile based films are identical. Several features are apparent. First, the α_a and γ

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relaxations, which have been observed by other workers (25-34), are seen in fig. (1c). The notation is chosen to be consistent with books on the subject (25,26), however, several other workers use different nomenclatures (28,30-34).

The α_a relaxation is associated with the glass transition. This is confirmed by the DSC results shown in fig. (1c). The γ relaxation is ascribed to small scale motion of the main chains, and has been variously attributed to a "crankshaft mechanism" (35,36), "3-bond" or "4-bond" motions (37,38), "chain end hydroxyl groups" (26), or the "$tg^+t \not\rightleftharpoons tg^-t$" transition (33). A consistent interpretation of the present results can be made in terms of the latter mechanism.

A third relaxation is apparent in fig. (1d) which is superimposed on the DC conductivity. The peak position is close to a mechanical relaxation peak reported by Connor et al. (29) or Kalfoglou (39) and thus probably corresponds to the α_c relaxation which is associated with the crystalline phase.

Evident at higher temperatures still is the solid-liquid transition of the pure PEO. The DSC peak occurs at a higher temperature than the conductivity anomaly. A major contribution to this effect is that the conductivity data were taken by slowly decreasing temperature and the DSC data are for rapidly increasing temperatures. Thus, the hysteresis is not surprising. Further, the DSC peak is about 5-10C higher than that reported by Kusy and Turner (40) for similar molecular weight samples. This is within the error of the present instrument but may imply that it is biased toward high temperatures, in this temperature range at least.

These features are to be compared with the following results for PEO complexed with various alkali metal thiocyanates.

3.2. PEO-AM(SCN)

The results for PEO complexed with some alkali metal thiocyanates are shown in figs. (2)-(5). The α_a relaxation which occurs at about 224K and 10,000 Hz in pure PEO is absent in all of the complexed materials. This is consistent with the present DSC measurements as no thermal anomalies are observed in the vicinity of 224K for any of the complexed samples.

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This indicates that no amorphous, pure PEO
exists in the complexed materials. The
remaining possibilities are crystalline PEO and
various forms of complexed PEO. The DSC results
rule out the presence of pure crystalline PEO
for PEO-LiSCN and PEO-KSCN as no thermal anomaly
is found where pure PEO is expected to melt (about
350K). For PEO-NaSCN there is an endotherm in ·
the region of 350K. This type of behavior has
previously been observed by Lee and Wright (5) in
PEO-NaSCN showing none of the x-ray patterns
characteristic of pure PEO. Therefore, in the
light of the results of Lee and Wright, and the
results for our lithium and potassium complexed
material prepared using the same procedures, it
is concluded that this endotherm is not due to
melting of pure PEO and that, in fact, all the
samples are fully complexed.

As regards the nature of the transition in
PEO-NaSCN and PEO-KSCN (endotherm at about 400K),
Lee and Wright attribute it to disording of the
complexed material within the network of chains
between the lamellae (their phase II). That
these materials are highly crystalline and thus
allow for interlamellae material is consistent
with the observations of Papke et al. (10). It
is noted that the dominant thermal features for
PEO-NaSCN and PEO-KSCN occur at higher
temperatures than the discontinuity in conductivity
for each material. The temperature difference is
due to the hysteresis effect and DSC calibration
error discussed above for pure PEO.

In contrast, PEO-LiSCN shows a very strong
glass transition which is observed at about 290K
as can be seen from the DSC results of fig. (2d).
In samples not heated above 340K (fig. (2d)),
there is a corresponding anomaly in the con-
ductivity. Samples taken to higher temperatures
do not exhibit this feature and in addition,
have a lower conductivity at all temperatures.
Based on the nature of the thermal anomaly and
the fact that the samples are rubbery at room
temperature, it is concluded that our PEO-LiSCN
is highly amorphous. It is suggested that the
amorphous character of the lithium complexed
material is due to the presence of water, since
the LiSCN was initially hydrated and attempts
to remove the water of hydration were only
partially successful. This conclusion is
consistent with the observations of Weston and
Steele (41) who find that polymers complexed
using "wet" solvents were amorphous while those
made using "dry" solvents were more crystalline.

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For the pure PEO, PEO-LiSCN, and PEO-NaSCN samples, the γ relaxation occurs at about 195K and 10,000 Hz and is similar in the three materials. The possibility that pure PEO is present in the complexed material has already been ruled out. Further, the intensity of the γ relaxation in the complexed materials is not diminished from that in pure PEO. Consequently, there appears to be no difference in the γ relaxation between pure PEO and PEO-LiSCN and PEO-NaSCN. These results must be reconciled

with the results of Parker et al. (4) who con-
clude from x-ray work that the chains in the
complexed materials are contracted. In this
regard, the ttg⁺ttg⁻ structure of the complexed
material due to Papke et al. (10) is relevant.
In fact, both the "tg⁺t $\rightleftharpoons$ tg⁻t" and "chain end
hydroxyl group" mechanisms would be expected to
be relatively unaffected by a shortening of
the chains. However, as shown below, only the
former mechanism is consistent with the results
for PEO-KSCN.

Parker et al. (4) also suggest that the
structure of the complexed material is a double
helix rather than two single chains. At first
sight, it would appear that the results of the
present work are inconsistent with a double
helix as it might be expected that the tg⁺t $\rightleftharpoons$
tg⁻t transition and hence the γ relaxation
should be affected more than is observed.
However, as these considerations are only
intuitive, the possibility of a double helix
cannot be ruled out. This is particularly
true since the considerations of Parker et al.
(4) help explain the results for PEO-KSCN.

As seen in fig. (4c), three peaks are observed
in PEO-KSCN in the region of the γ relaxation.
Three peaks are observed in PEO-KSCN prepared
with both methanol and acetonitrile thus ruling
out solvent effects. The explanation for this
is that the lithium and sodium ions fit easily
within the helical tunnels while potassium,
being larger, produces more severe local
distortions in the polymer chain. The distortions
in turn introduce an inequivalence between the
potential wells or barriers associated with the
γ relaxation. In fact, Parker et al. (4) have
pointed out that "calculations show that lithium
and sodium ions may be readily accommodated within
the cavities but that potassium ions are barely
accommodated and require that two of the C-C bonds
adopt rotation angles within the trans domain."
As the γ relaxation is associated with the C-O
bond, just this difference may be responsible for
the difference in the relaxation spectrum between
PEO-KSCN and the other alkali metal thiocyanates.
Further, the differences in the relaxation spectrum
are probably correlated with the differences in the
IR spectra for PEO-NaSCN and PEO-KSCN reported by
Papke et al. (10).

Finally, the results for PEO-KSCN rule out the
"chain end hydroxyl mechanism" for the γ relaxation
since it is difficult to understand how the

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cations could have such a significant effect on the chain ends for PEO-KSCN but not for PEO-LiSCN or PEO-NaSCN.

4. SUMMARY

In summary, then, several results have been obtained by a complex admittance and DSC study of pure PEO and PEO complexed with various alkali metal thiocyanates:

(1) The dielectric constant of the complexed materials is found to be greater than that for pure PEO.

(2) A discontinuity in the conductivity is found which decreases in temperature as the size of the cation decreases. Each discontinuity is correlated with a thermal anomaly.

(3) PEO-LiSCN is amorphous at low temperatures while PEO-NaSCN and PEO-KSCN are highly crystalline. It is suggested that the amorphous phase is easier to form in the presence of water.

(4) For PEO-LiSCN and PEO-NaSCN, the position of the γ relaxation is about the same as for pure PEO. For PEO-KSCN three relaxations are observed in the region of the γ relaxation. These results are consistent with a $tg^+t \rightleftarrows tg^-t$ relaxation of a helical structure where the cations reside within the helical channels at low temperatures.

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Fig.1. Pure PEO. The dielectric data are: dashed curve 100 Hz; solid curve 1000 Hz; chain link curve 10,000 Hz. The dielectric data are for decreasing temperatures only and straight lines connect the datum points. The DSC results are for increasing temperatures at a rate of 10C per minute. (a) ϵ' vs. T(K) (b) Log(ϵ') vs. $1000/T(K^{-1})$ (c) ϵ'' vs. T(K); DSC discontinuity height of 2 units (abritrary) (d) Log($\sigma(\Omega\text{-cm})^{-1}$) vs. $1000/T(K^{-1})$; DSC peak height of 36 units.

1a

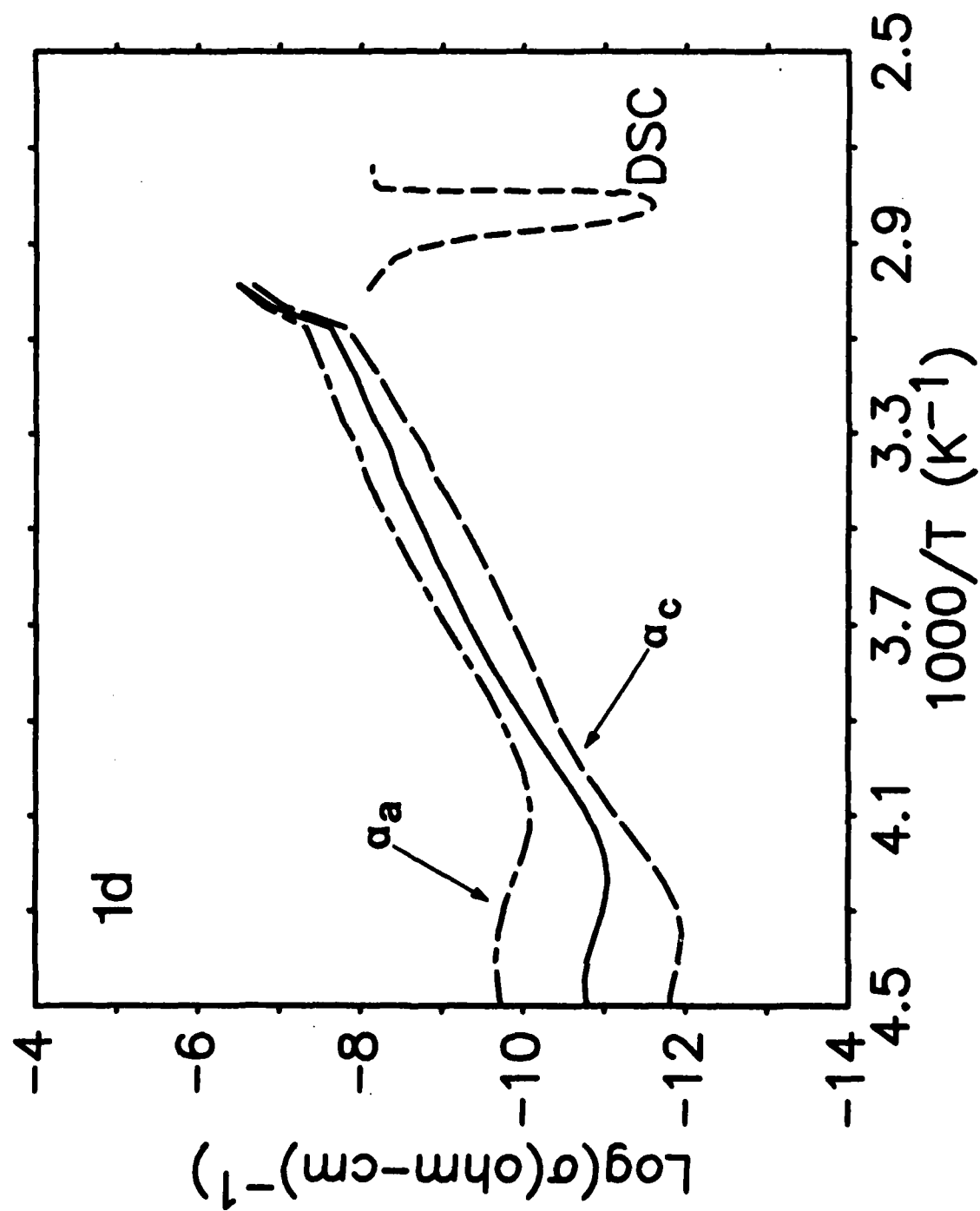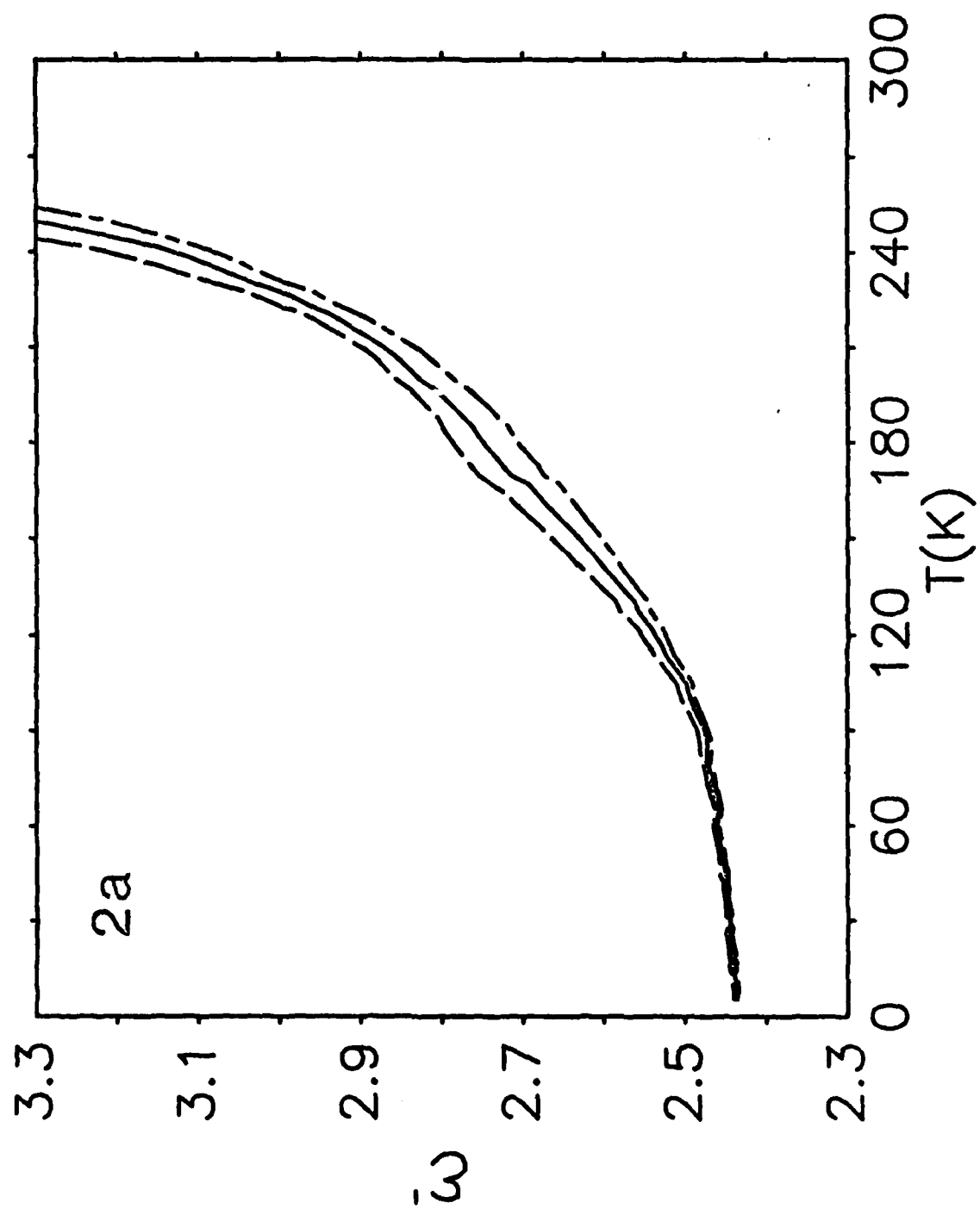Figure 1b. Plot of Log (ε') versus 1000/T (K⁻¹).

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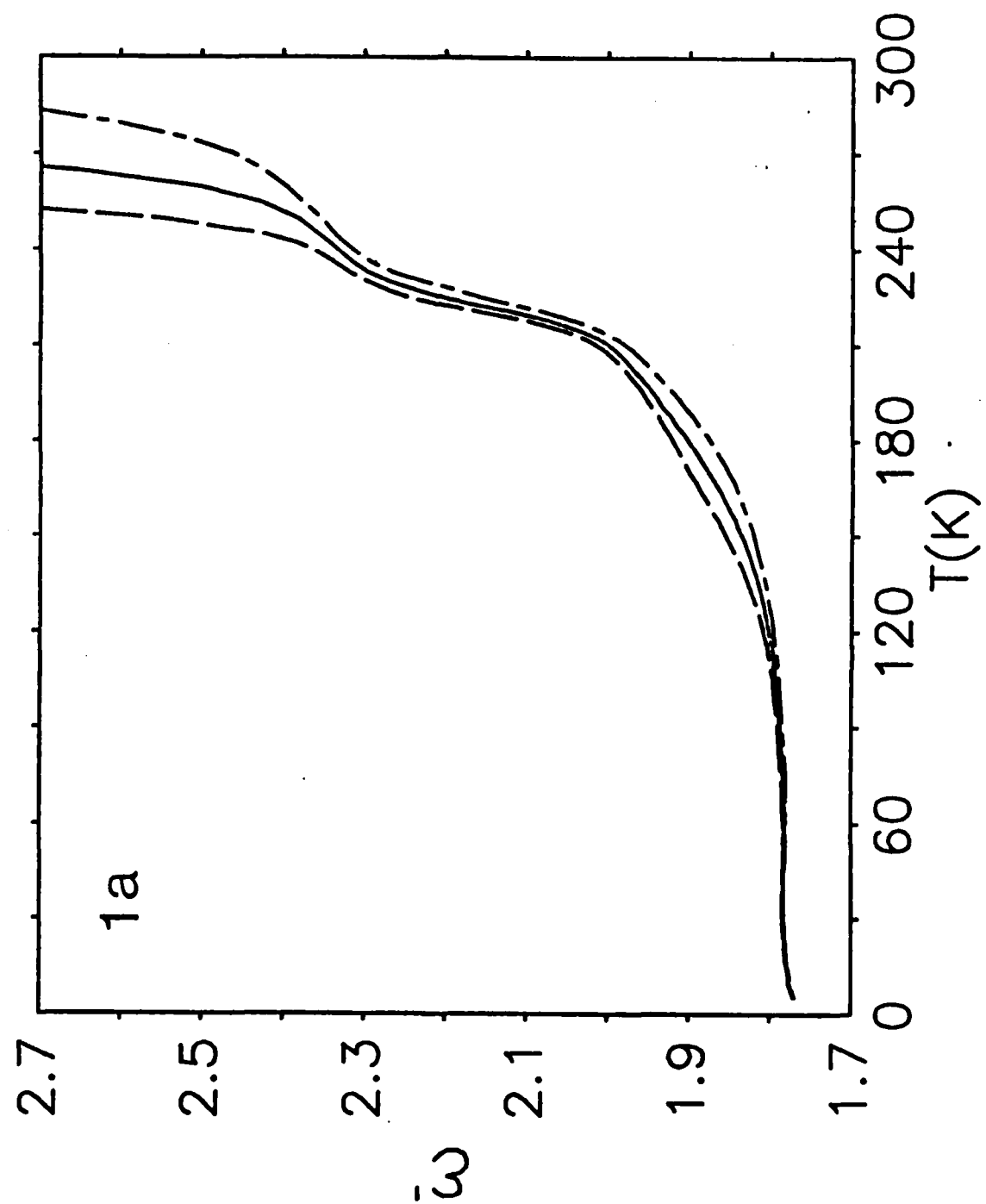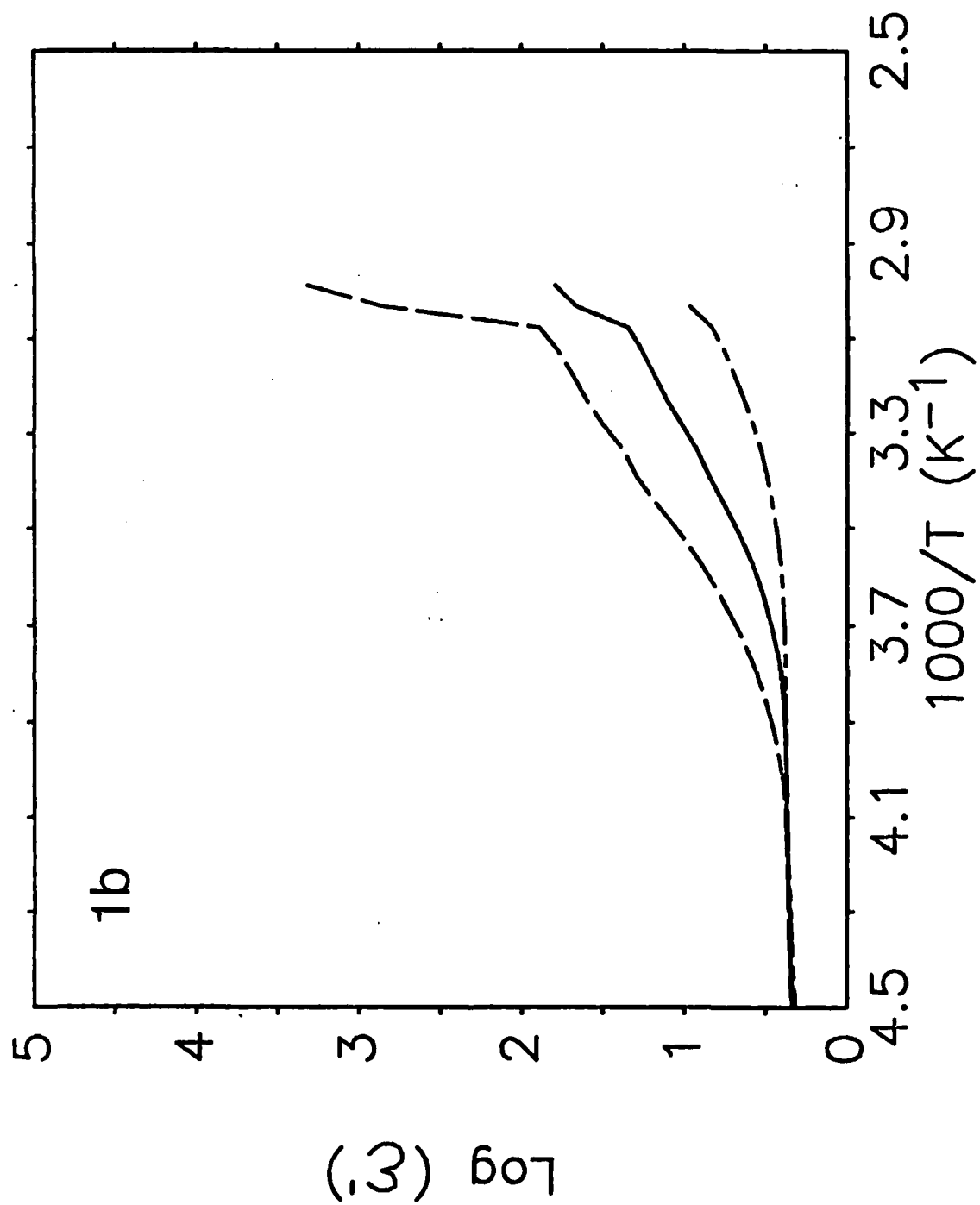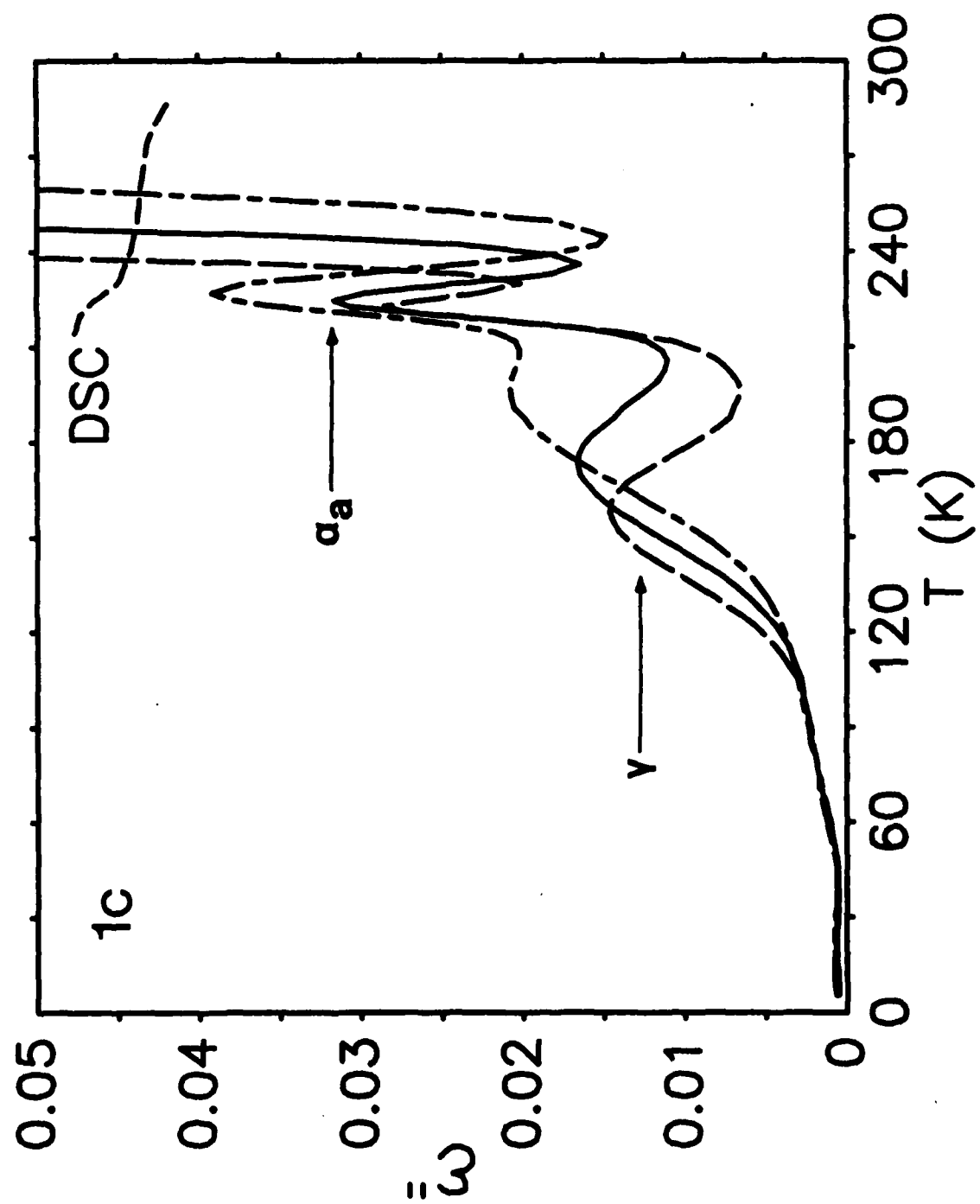
Fig. 2. PEO_5-LiSCN. The dielectric data are: dashed curve 100 Hz; solid curve 1000 Hz; chain link curve 10,000 Hz. The dielectric data are for decreasing temperatures only and straight lines connect the datum points. The DSC results are for increasing temperatures at a rate of 10C per minute. (a) ϵ' vs. T(K) (b) $Log(\epsilon')$ vs. $1000/T(K^{-1})$ (c) ϵ'' vs. T(K) (d) $Log(\sigma(\Omega\text{-cm})^{-1})$ vs. $1000/T(K^{-1})$; DSC discontinuity of 5 units.

19

2a

$\bar{\omega}$

T(K)

Figure caption area (rotated):

2b

Y-axis: Log($\mathcal{E}'$)

X-axis: 1000/T (K^{-1})

2c

$\tilde\varepsilon$
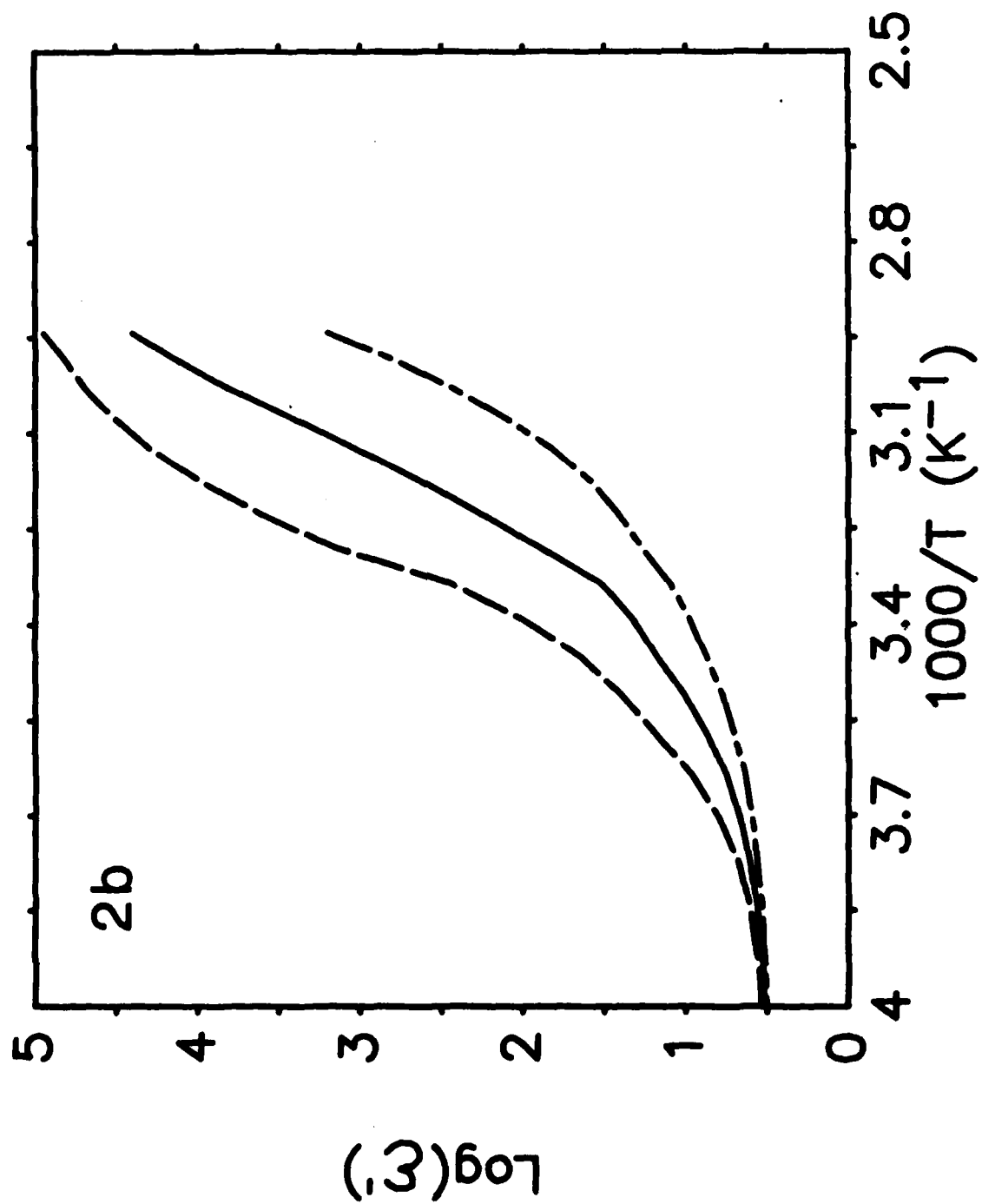
T(K)

Fig. 3. $PEO_{4.5}$-NaSCN. The dielectric data are: dashed curve 100 Hz; solid curve 1000 Hz; chain link curve 10,000 Hz; + data of Wright (2). The dielectric data are for decreasing temperatures only and straight lines connect the datum points. The DSC results are for increasing temperatures at a rate of 10C per minute. (a) ϵ' vs. T(K) (b) $Log(\epsilon')$ vs. $1000/T(K^{-1})$ (c) ϵ'' vs. T(K) (d) $Log(\sigma(\Omega\text{-cm})^{-1})$ vs. $1000/T(K^{-1})$; DSC peak height of 2 units.
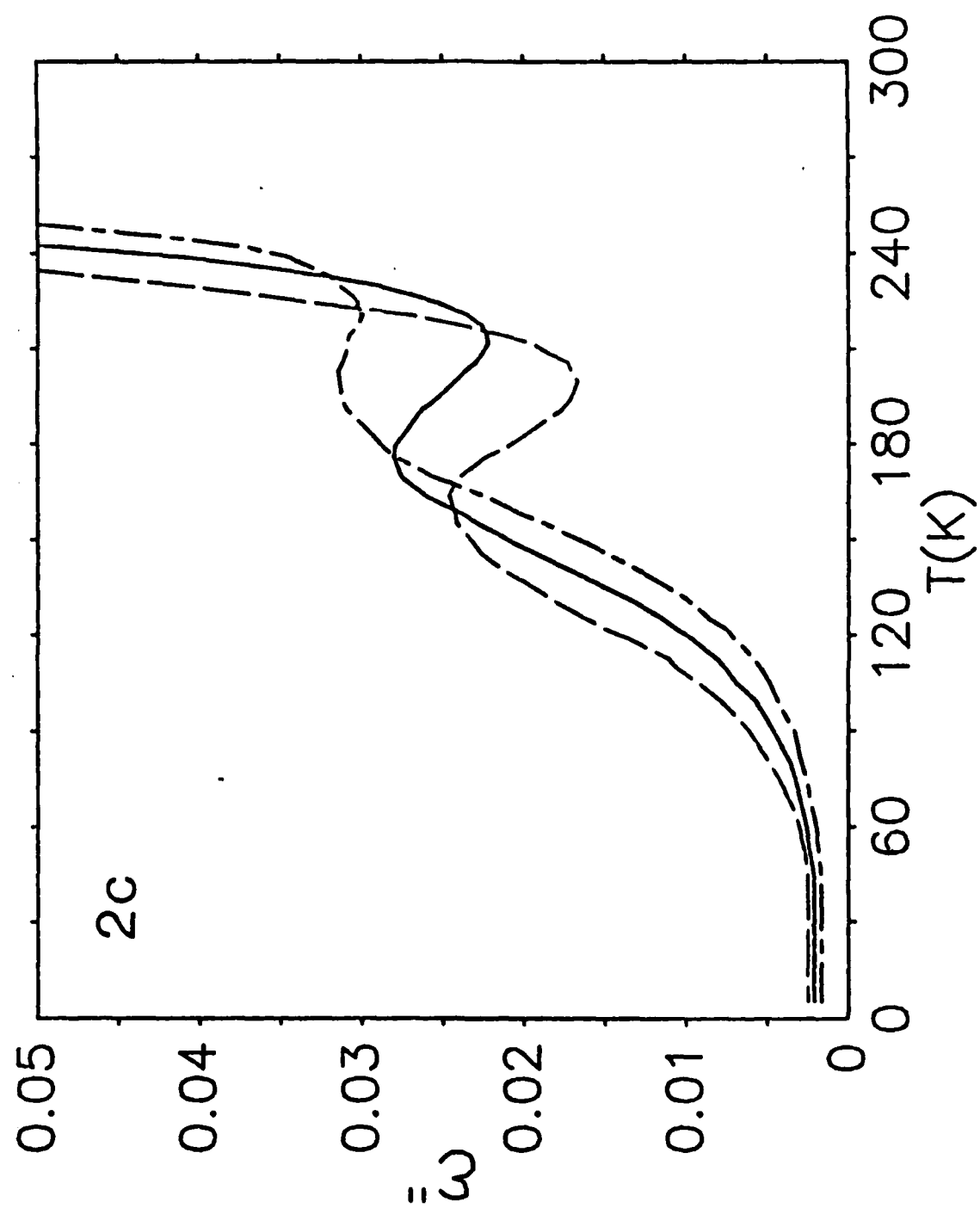
3a

$\bar{\varepsilon}$

T(K)

3b

Log(ε')

1000/T (K⁻¹)

3c

$\bar{\varepsilon}_{11}$

T(K)

Figure 3d. Plot of $\mathrm{Log}(\sigma(\mathrm{ohm\text{-}cm})^{-1})$ versus $1000/T$ (K^{-1}), labeled DSC.
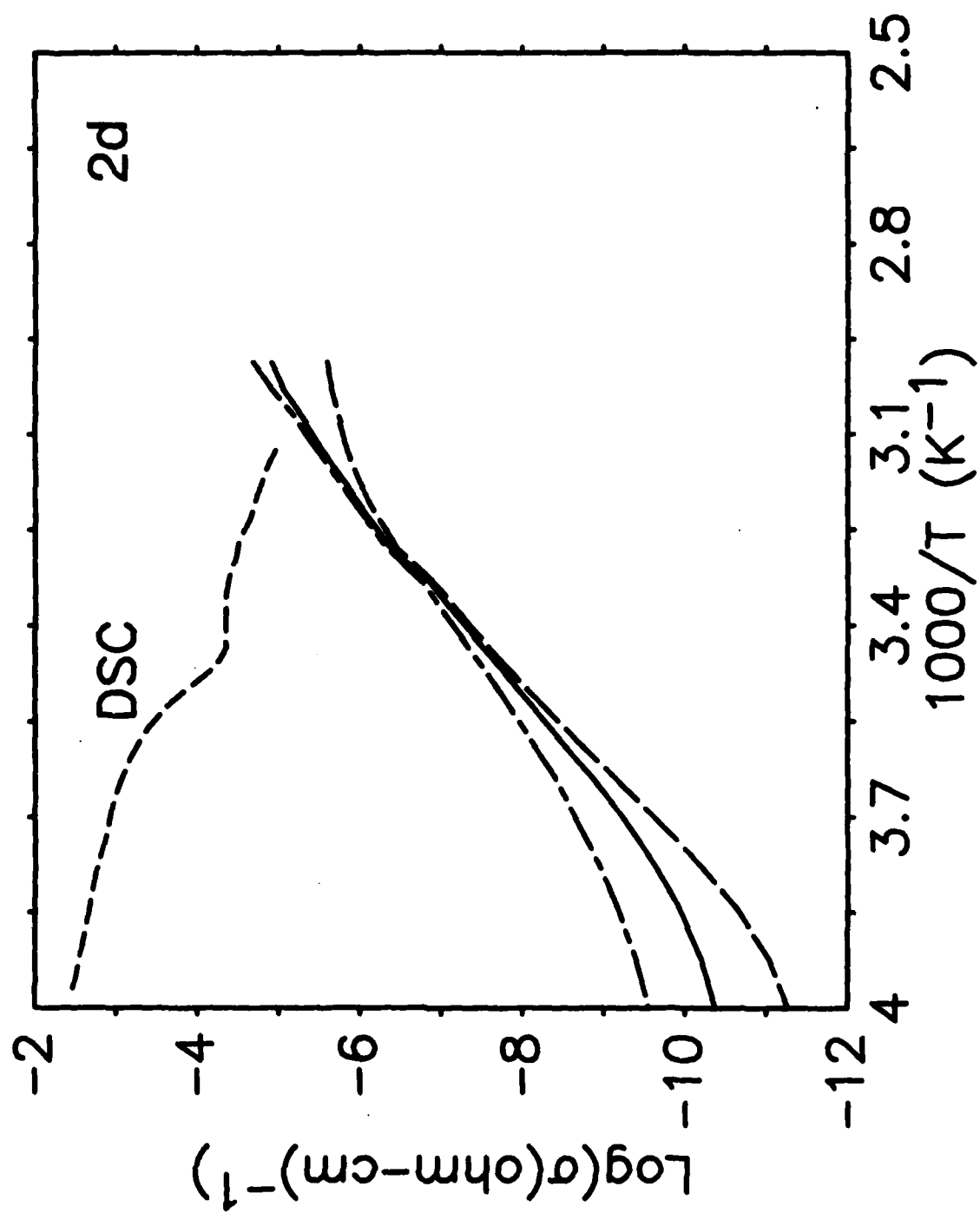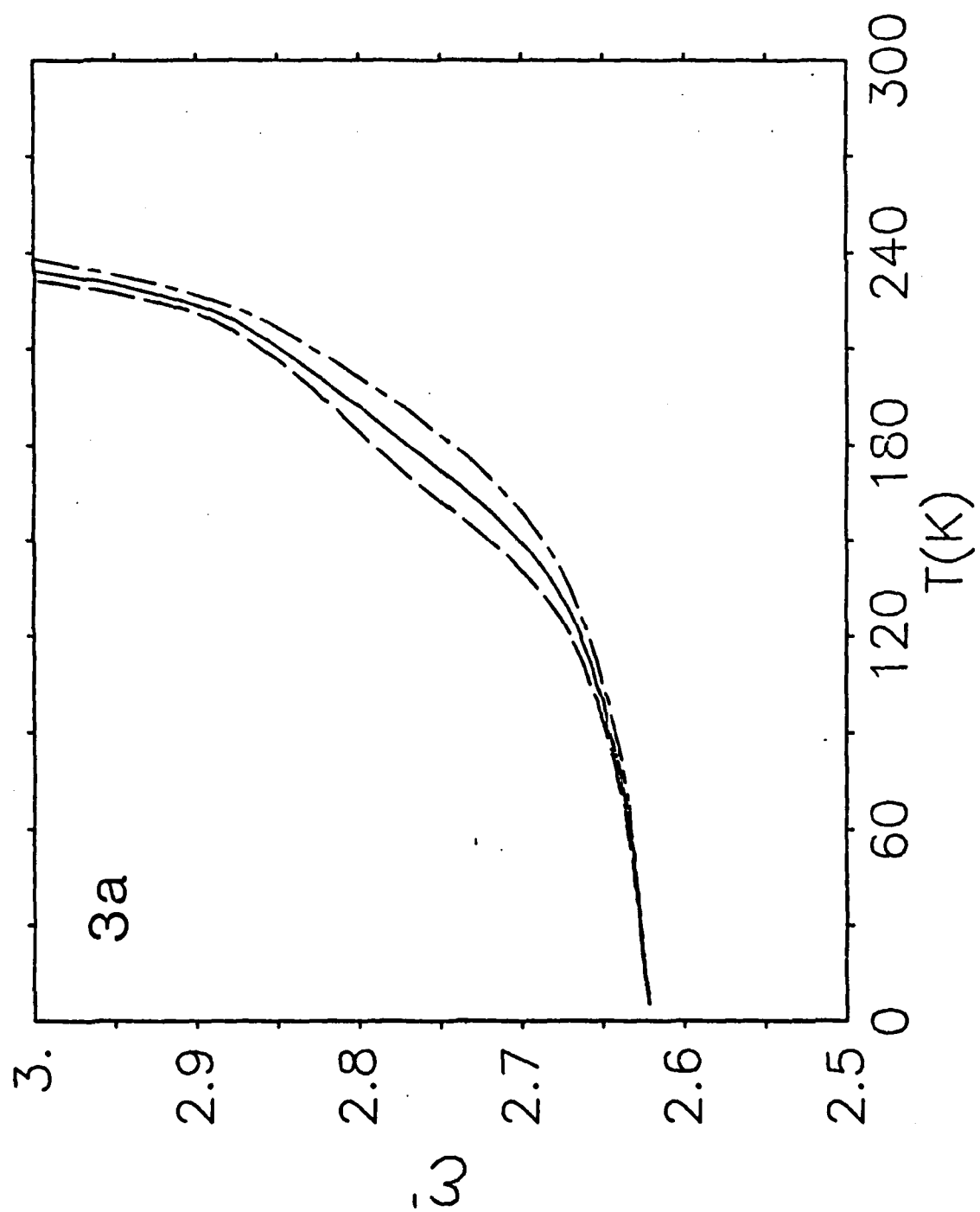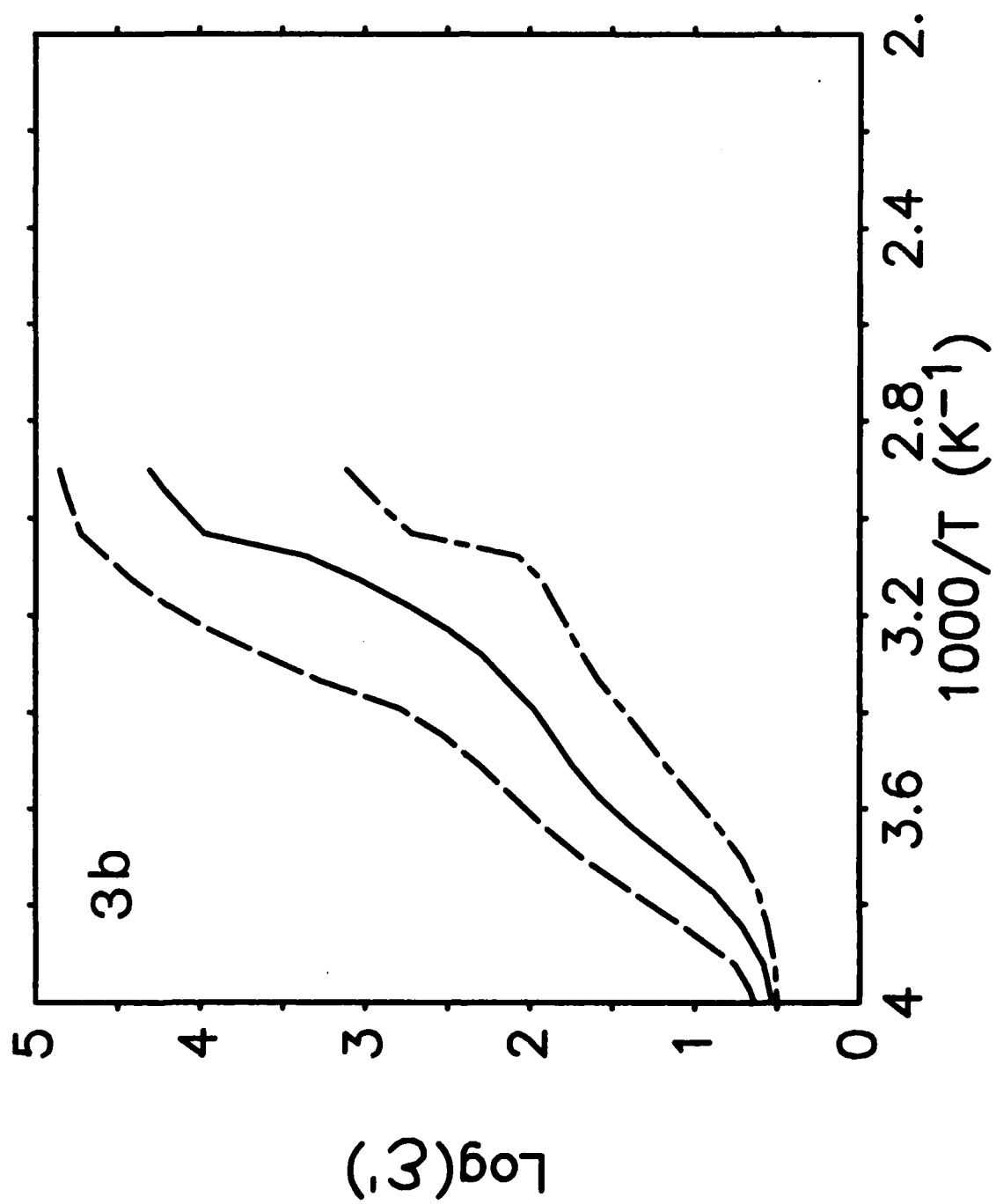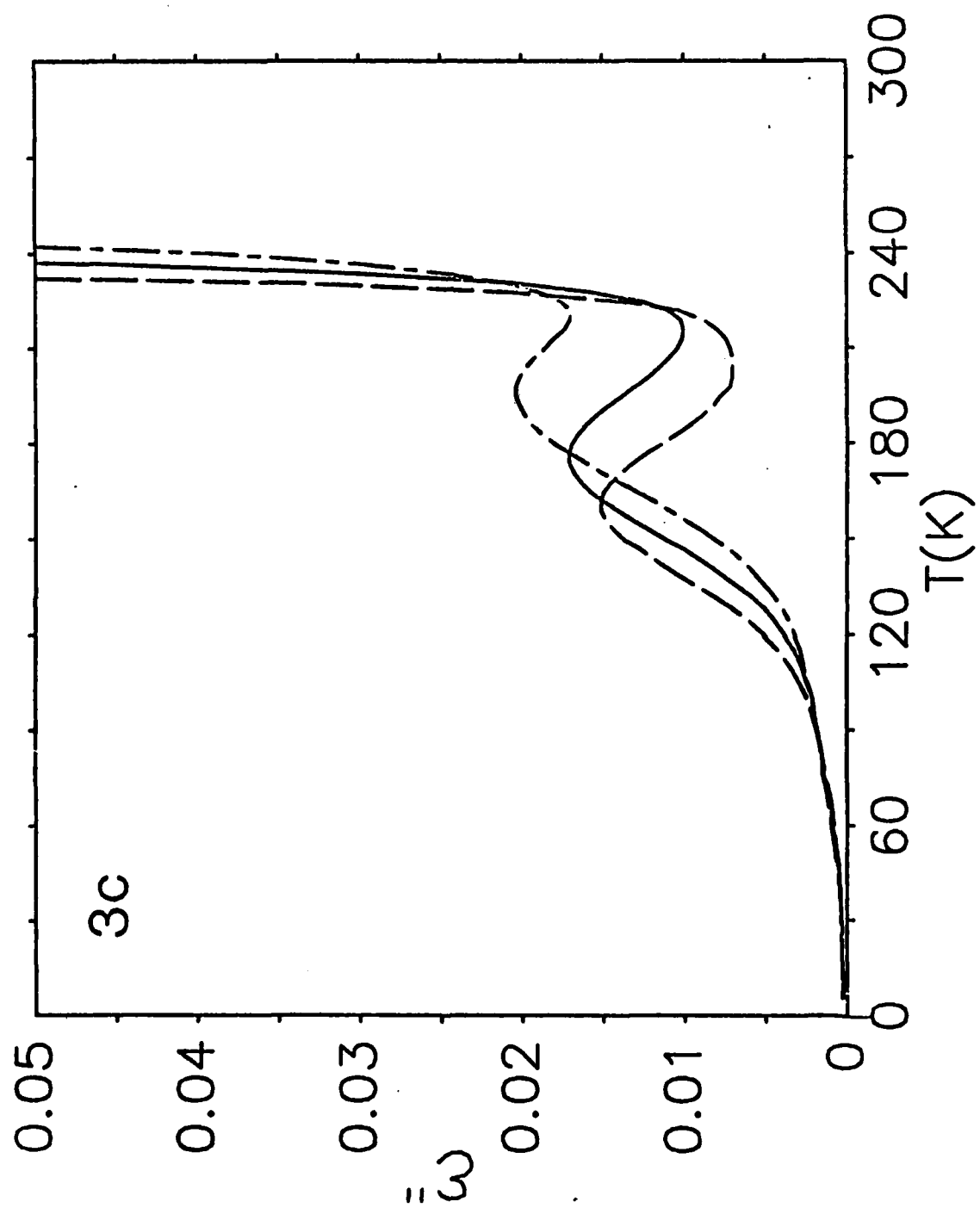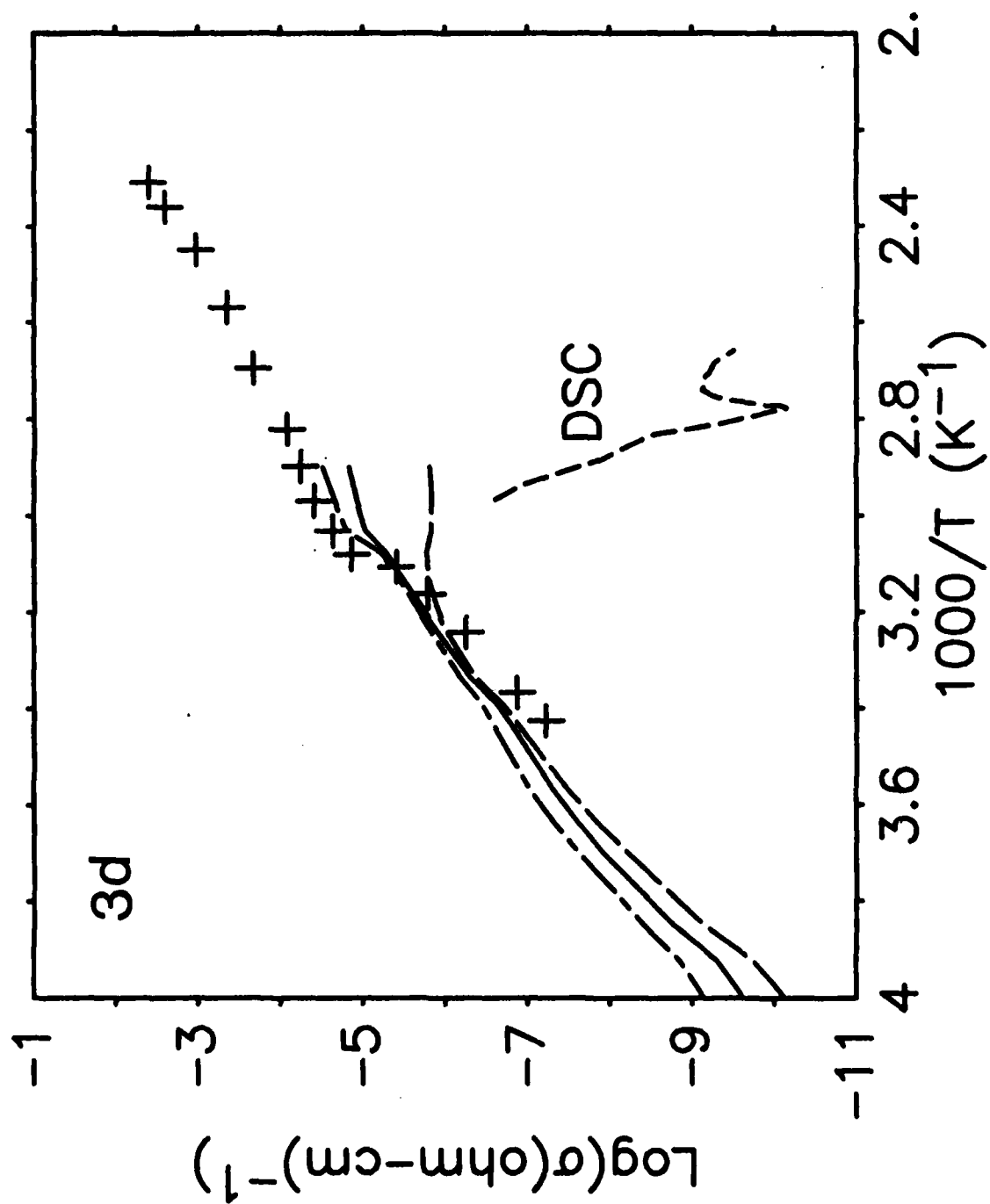
Fig. 4. PEO$_{4.5}$-KSCN. The dielectric data are: dashed curve 100 Hz; solid curve 1000 Hz; chain link curve 10,000 Hz; + data of Wright (2). The dielectric data are for decreasing temperatures only and straight lines connect the datum points. The DSC results are for increasing temperatures at a rate of 10C per minute. (a) ϵ' vs. T(K) (b) Log(ϵ') vs. 1000/T(K^{-1}) (c) ϵ'' vs. T(K) (d) Log($\sigma(\Omega\text{-cm})^{-1}$) vs. 1000/T(K^{-1}); DSC peak height of 28 units.

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4a

$\bar{\omega}$

T(K)

Log(ε')

1000/T (K^{-1})

4b

2. 2.4 2.8 3.2 3.6 4

0 1 2 3 4 5

4c

ε''

T(K)

4d

DSC

$Log(\sigma(ohm-cm)^{-1})$
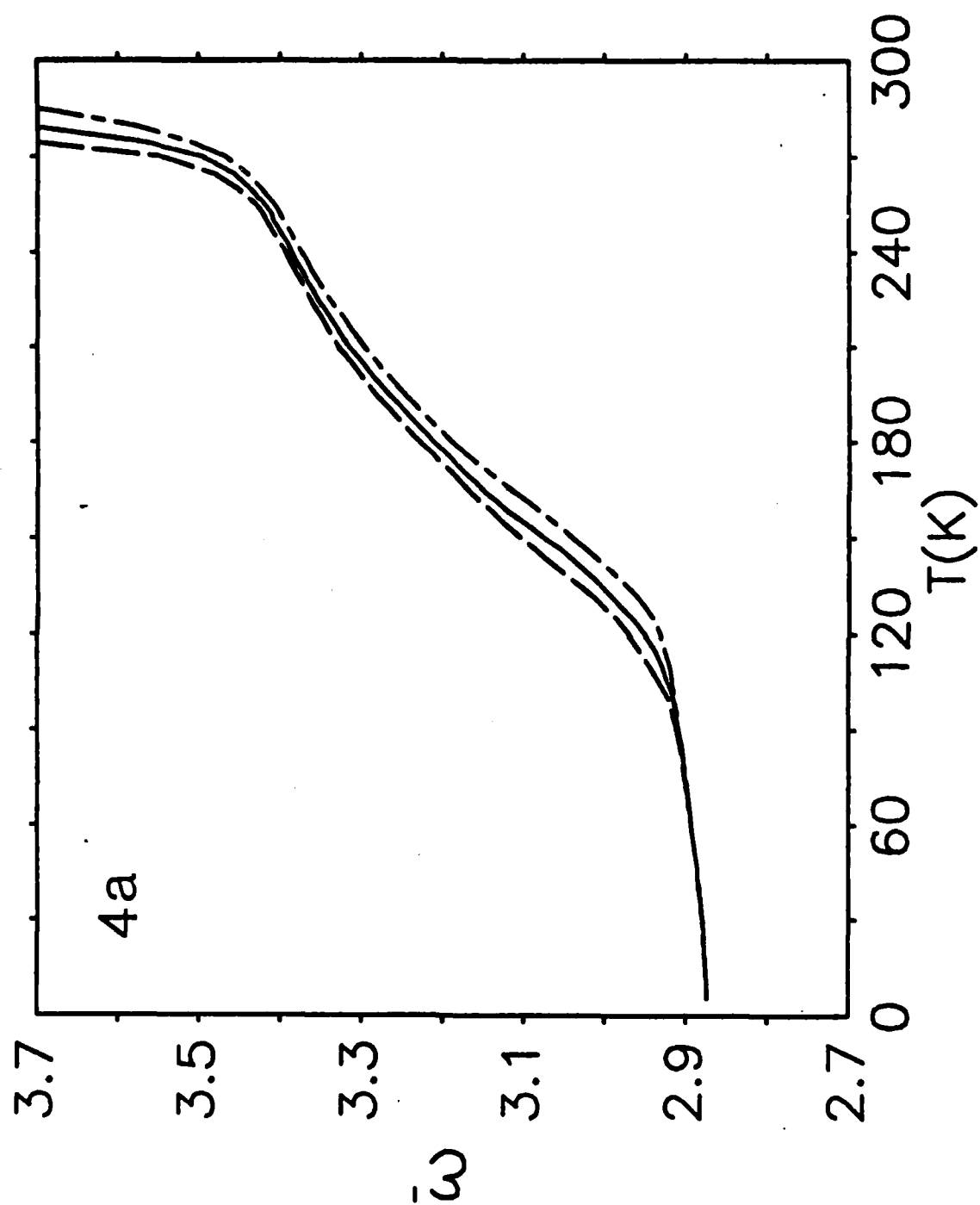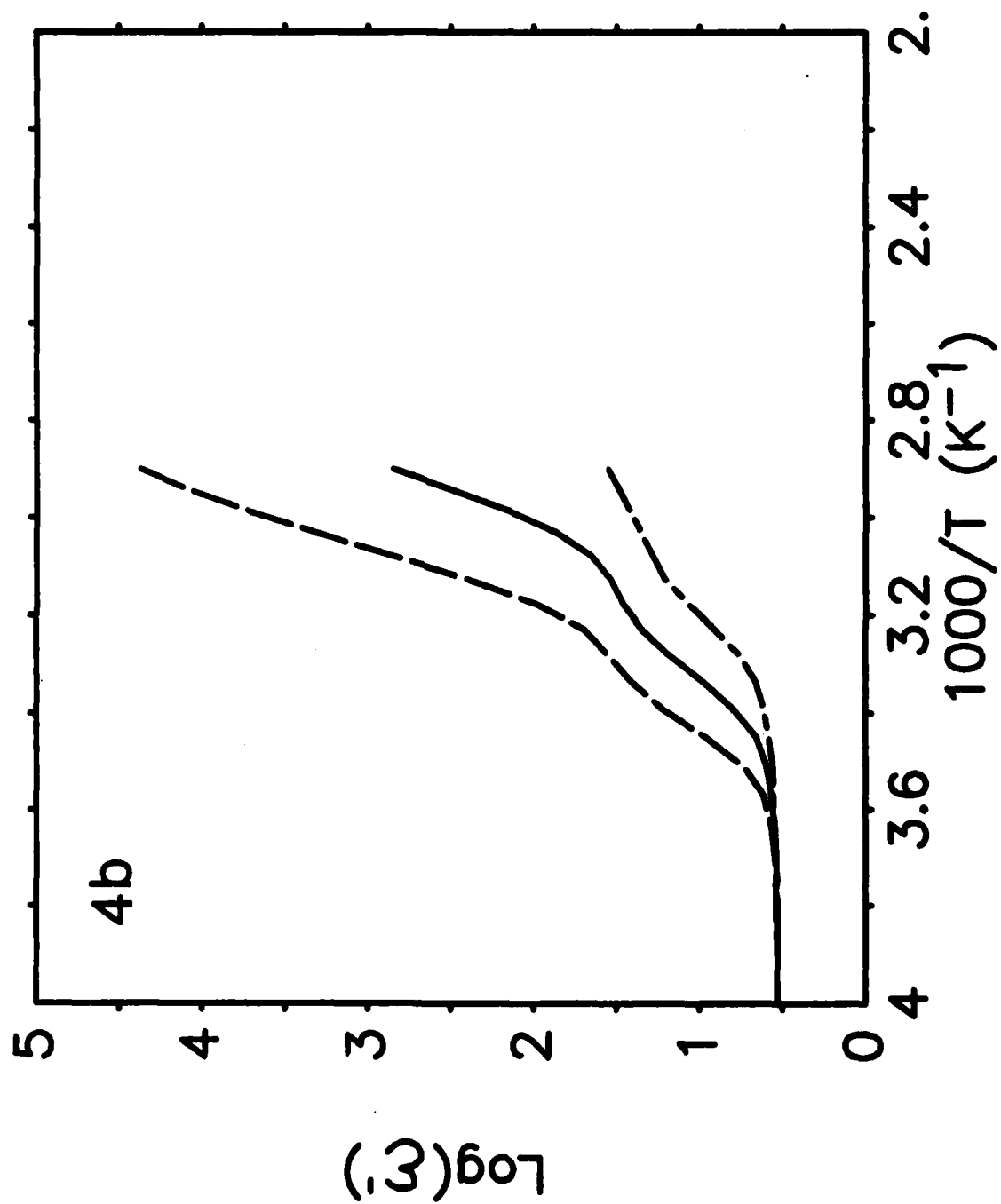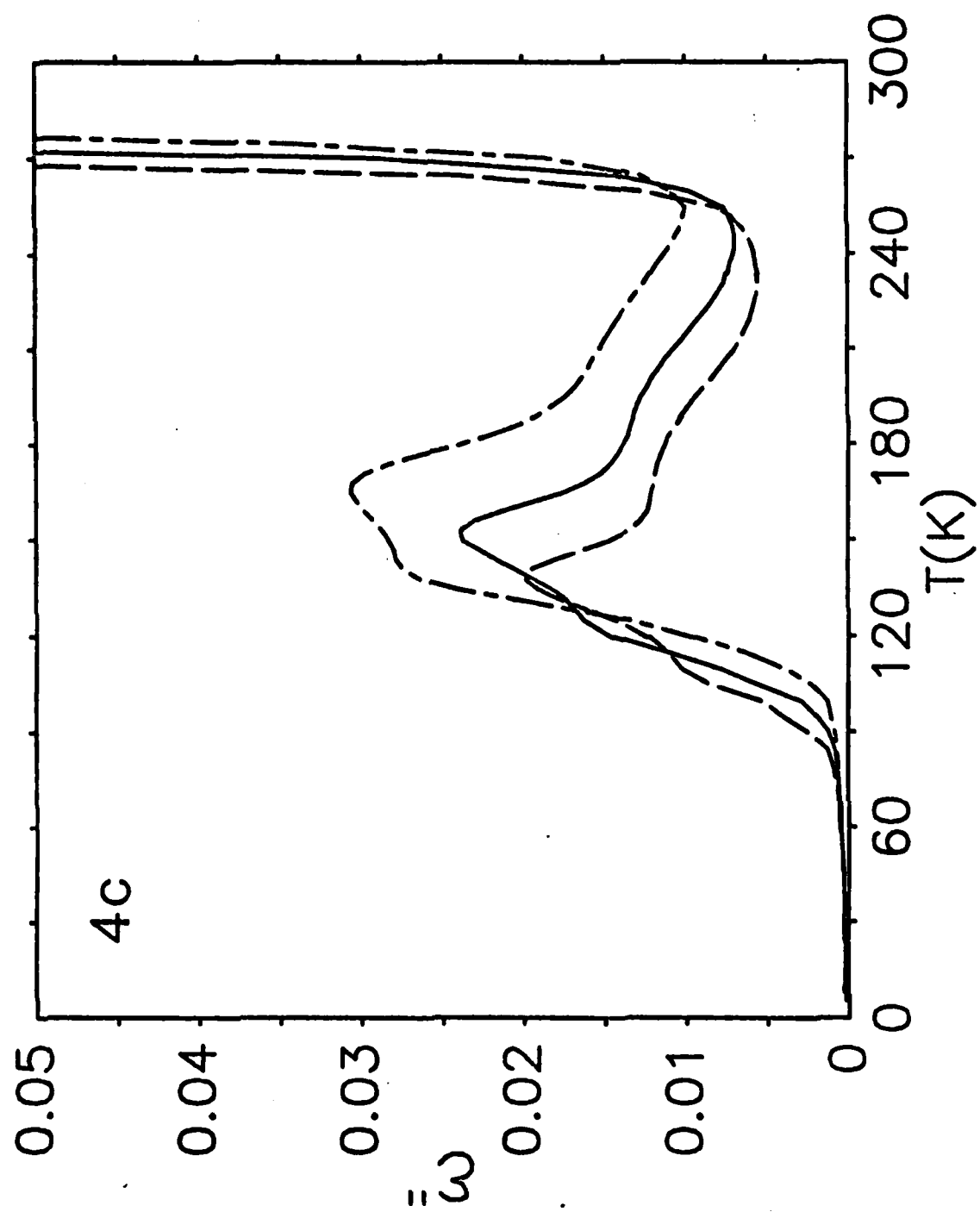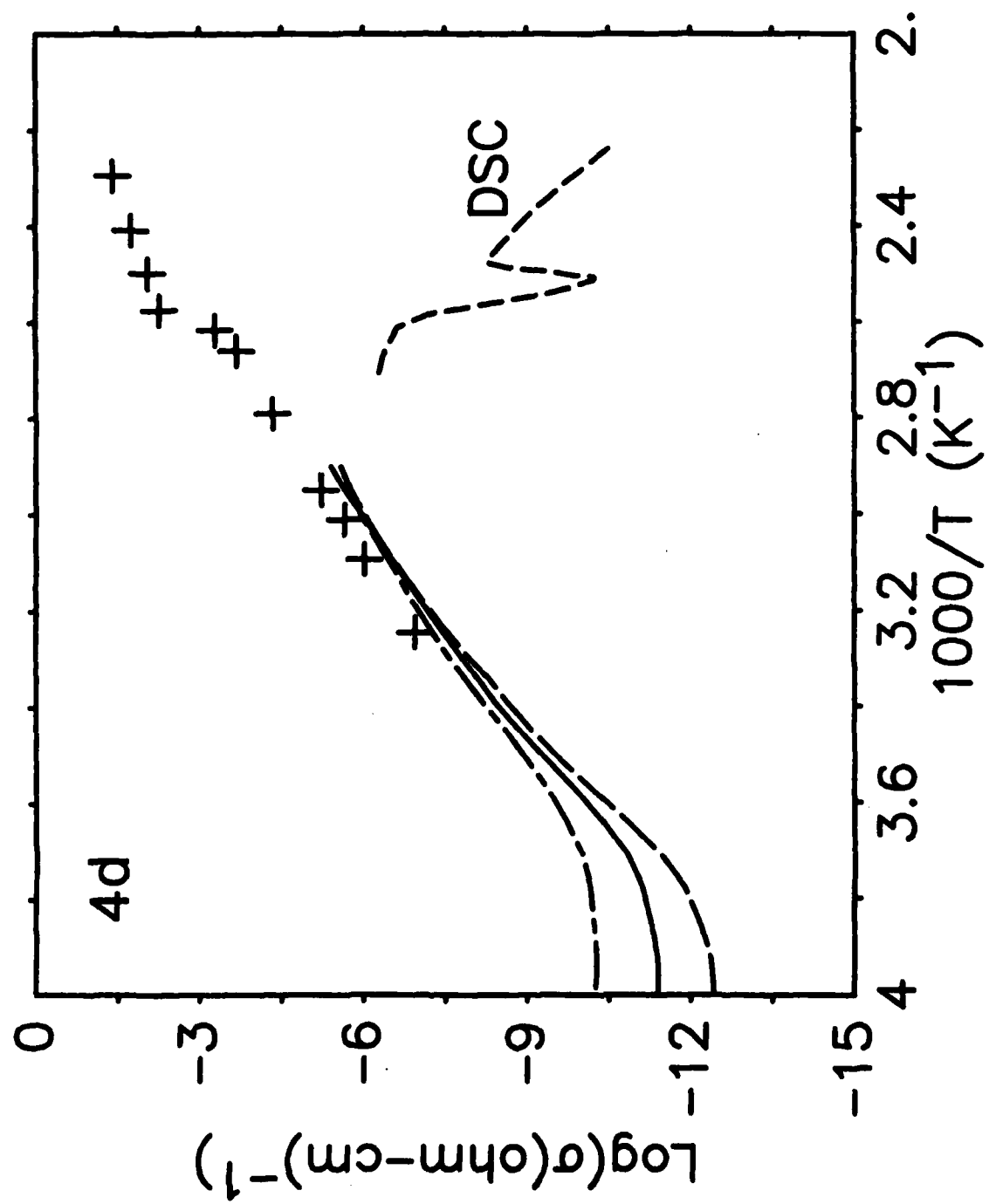
$1000/T$ (K^{-1})

Fig. 5. PEO$_{4.5}$-KSCN. (a) ε'' vs. T(K) at 10^3 Hz. The datum points are represented by triangles. (b) Log($\sigma(\Omega\text{-cm})^{-1}$) vs. 1000/T(K^{-1}) at 10^3 Hz. x – Increasing temperature; o – Decreasing temperature. Straight lines connect the datum points.

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5a

ϵ_{II}

T(K)

5b
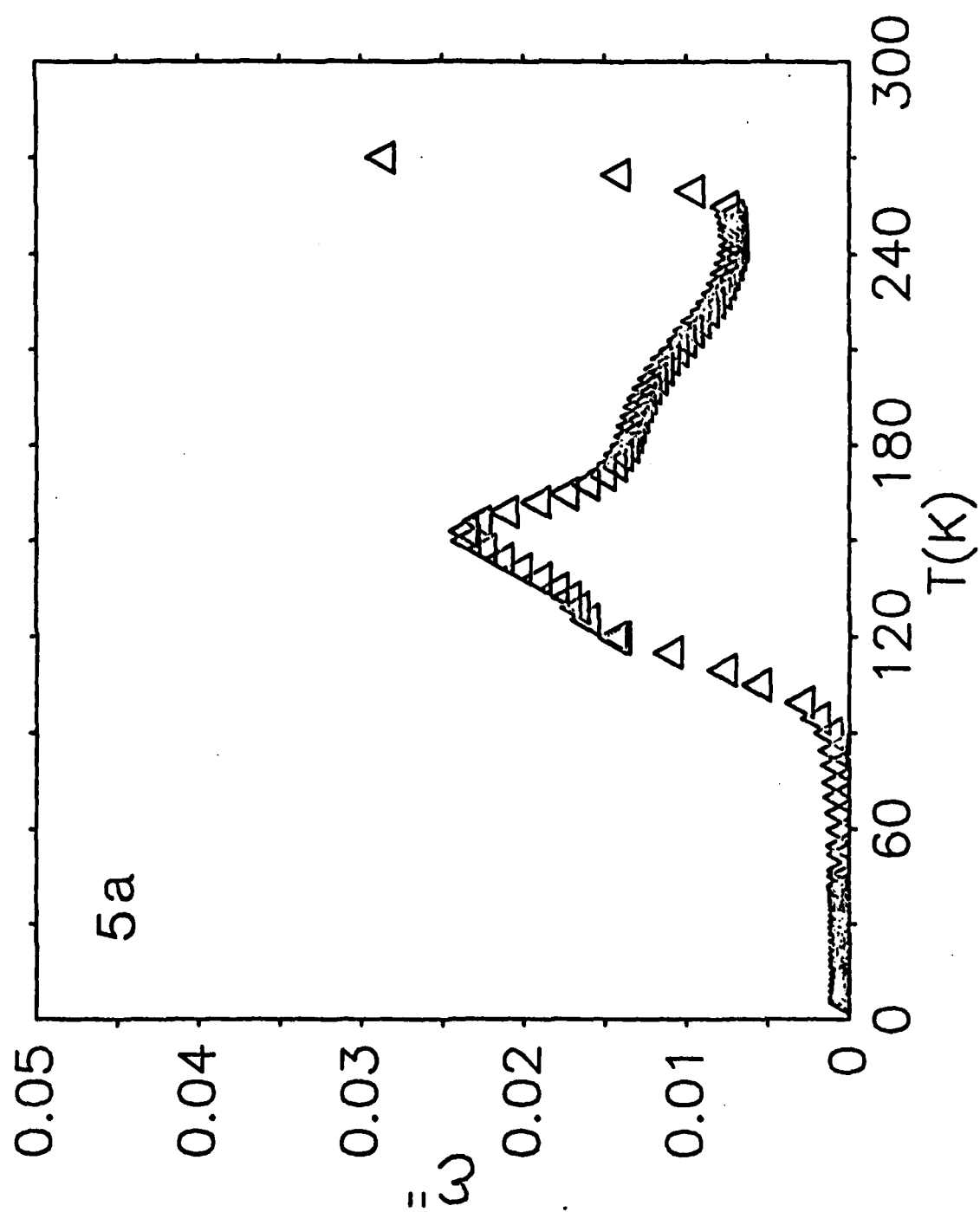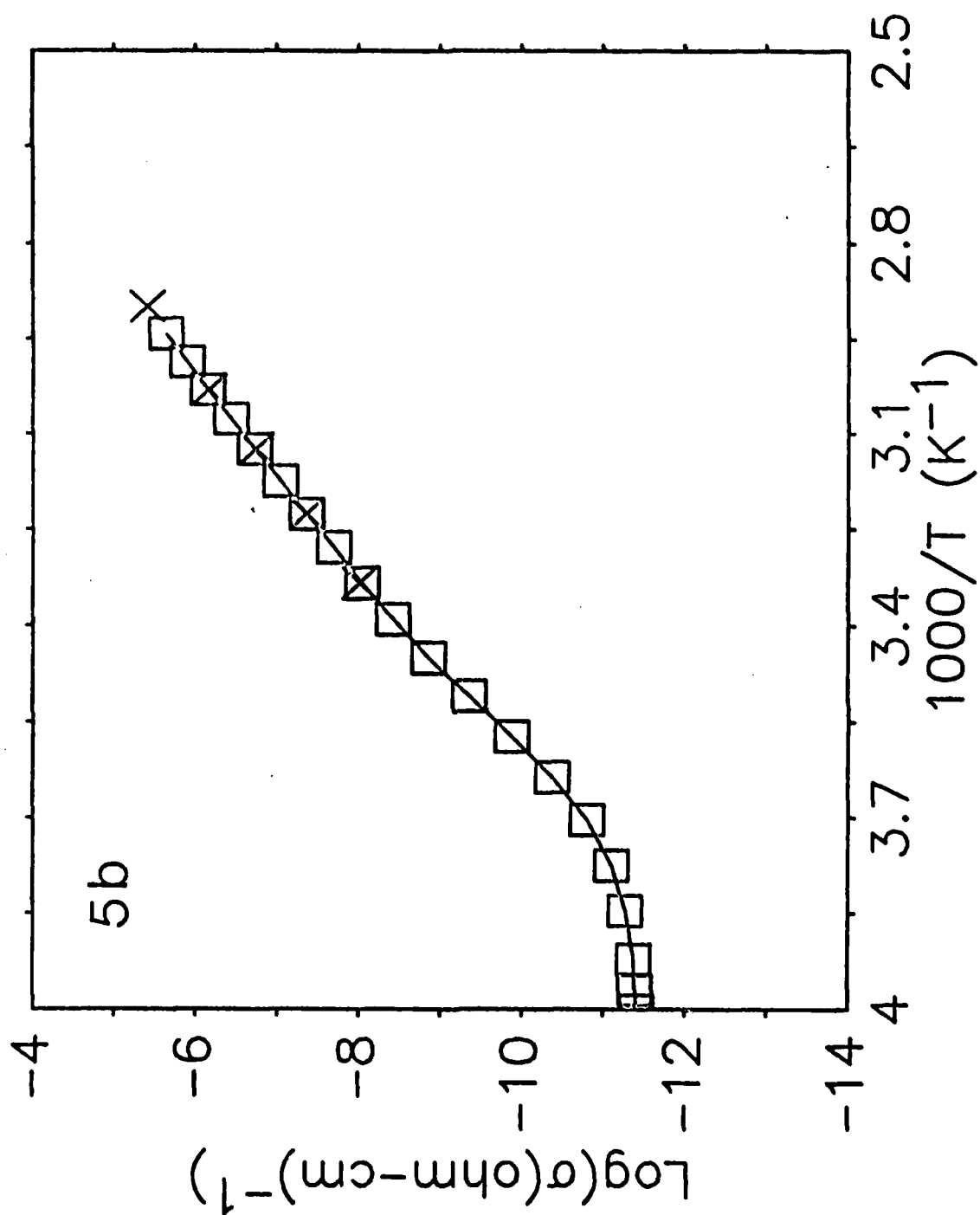
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Audio frequency complex admittance and DSC studies have been performed on pure poly(ethylene oxide)(PEO) and PEO complexed with alkalai metal thiocyanates over the temperature range 5.5-380K. The dielectric constant of the complexed materials is found to be greater than for pure PEO. A discontinuity in the conductivity is found which increases in temperature as the size of the cation increases. In every case, the discontinuity is associated with a feature in the DSC results. Next, some evidence is given

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that water may enhance the formation of amorphous complexed PEO. In pure PEO, α_a and γ relaxations are observed in good agreement with previous work. A thermal anomaly is found corresponding to α_a. In addition, α_c is identified in pure PEO. Very little difference is found for the γ relaxation between pure PEO and PEO-LiSCN and PEO-NaSCN. For PEO-KSCN, three distinct peaks are found in the γ relaxation region. These results are consistent with a $tg^+t \rightleftarrows tg^-t$ transition interpretation for γ where the cations reside within the helical channels at low temperatures.